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METHOD FOR PRODUCING CHLORINE DIOXIDE AND ITS USE

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Addition to: 198 46 258.1

The following data are taken from documents submitted by the applicant.

Summary

The invention concerns a method for water treatment and/or disinfection of water using electrolytically produced chlorine dioxide.

Description

[0001]

This application is an addition to DE 198 46 258.1. This invention concerns a method for water treatment and/or disinfection of water using electrolytically produced chlorine dioxide.

[0002]

Because of its bactericidal and fungicidal effect, chlorine dioxide is suitable for water preparation. In addition, it is used industrially on a large scale as a bleaching agent.

[0003]

Chlorine dioxide is produced industrially through chemical reduction of chlorate, for example with sulfur dioxide, hydrochloric acid or chlorides, nitrogen dioxide or sulfuric acid. (See, for example, Ullman's Encyclopedia of Industrial Chemistry, Vol. 9, p. 550 to 551). Chlorine dioxide can also be produced by the chlorite-chlorine process and from sodium chlorite using chlorine as well as from sodium chlorite and acetanhydride.

[0004]

Chlorine dioxide is an unstable, non-storable gas that decomposes in an explosive fashion and must be produced on site in special plants as needed. The chlorine dioxide that is formed usually undergoes oxidation reactions. Chlorine dioxide is explosive both as a concentrated gas and in liquefied form.

[0005]

Moreover, it is known that according to legal requirements for drinking water and for public swimming pools a clearly defined microbiological water quality must be maintained. In most cases drinking water or swimming pool water is treated by means of chlorine or related byproducts such as chlorine dioxide.

[0006]

Because of the danger and environmental pollution that exists in the production, storage and transport of chlorine and also chlorine dioxide, there is a need for alternatives to these products or production of chlorine compounds that do not threaten the environment, so that these compounds can be produced and immediately used directly where they are required.

[0007]

It is also known that hypochlorous acid can be produced electrolytically at the point of use, but technically expensive equipment and costly maintenance are required. Most of these "hypochlorous acid processes" are only intended to be used in a closed water system, and about 4 to 7 kg of salt has to be dissolved per cubic meter of water. In the "hypochlorous acid process" sodium chloride is converted to hypochlorite, which then acts as a disinfectant. Besides the large amount of salt that is required here, the salt taste that arises with this process is a great disadvantage.

[0008]

Disadvantages of the known methods and the use of chlorine were the threat to health, the change of flavor of the water, the danger of corrosion of said metallic parts and costly maintenance.

[0009]

DE 31 18 795 A1 describes a method for producing chlorine dioxide by electrolysis of a chlorite solution, where the chlorite solution is used in a concentration from 10 to 40 g/L. With this method a chlorine dioxide/air mixture is obtained as product and can subsequently be used for the intended use.

[0010]

The disadvantages and dangers connected with the handling of explosive chlorine dioxide also arise with this method.

[0011]

The objective of the invention therefore was to make available a method for water treatment and/or disinfection that at least partially remedies the above disadvantages.

[0012]

This objective is solved in accordance with the invention by a method for water treatment and/or water disinfection using chlorine dioxide, which is characterized by the fact that chlorine dioxide is electrolytically produced in the water to be treated from chlorite and/or chlorate, which are present in a preset concentration from 0.1 to 5 ppm.

[0013]

In contrast to the prior art, in which chlorine dioxide was first produced as product and the separately produced chlorine dioxide was then introduced or inoculated into the water to be treated, with the method in accordance with the invention the chlorine dioxide is produced directly in situ in the water that is to be treated. The disadvantages connected with the product chlorine dioxide in gaseous or concentrated form can be avoided in this way.

[0014]

Surprisingly, it was found that chlorine dioxide can be electrolytically produced in situ from highly dilute chlorite solutions and/or chlorate solutions. The concentration of chlorite and/or chlorate in the water to be treated is, in accordance with the invention, from 0.1 to 5 ppm

(parts per million with respect to weight and calculated as sodium chlorite or sodium chlorate), thus the chlorite and/or chlorate are present in an amount from 0.1 to 5 g/m^3 water. Preferably, the chlorite and/or chlorate is used in an amount from 0.5 to 1.5 ppm. These amounts are lower, by orders of magnitude, than the amounts of chlorite used to produce a gaseous chlorine dioxide product in the known methods, for example in DE 31 18 795 A1. It is surprising that electrolysis of chlorite and/or chlorate to chlorine dioxide in such small concentrations is possible at all. An important advantage of the method in accordance with the invention is that a disinfectant action can be achieved directly in the water to be treated. The preparation of explosive chlorine dioxide (ClO_2) and its handling or subsequent dispensing into the water to be treated are thus not necessary.

[0015]

The method in accordance with the invention using chlorite and/or chlorate to form chlorine dioxide is advantageous compared to the use of sodium chloride, from which hypochlorite is electrolytically formed, since it is considerably more efficient and has practically no deleterious side effects. Moreover, when sodium chloride is used, clearly higher concentrates are necessary for successful electrolysis. In the amount of 0.1 to 5 ppm that is used, which is clearly lower than the amount of salt needed for electrolysis of chloride, the chlorite and/or chlorate are nontoxic and, in the amount formed from them, chlorine dioxide also does not represent a problem. The disinfected water in accordance with the invention does not have any salt taste, it does not burn the mucosa, and an algicide is also not necessary.

[0016]

According to the invention, the chlorine dioxide used for water treatment and/or water disinfection is produced electrolytically. Here chlorine dioxide is produced from chlorite and/or chlorate in the water to be treated with high efficiency in an electrolysis device that is familiar to the specialist. With chlorine dioxide an excellent disinfection of the treated water, for example drinking water or swimming pool water, is possible even at high pH values, and a long lasting bacteriostatic protection can be achieved. Other advantages of the method in accordance with the invention are lower costs compared to the known chlorine dioxide production processes, production directly on site, safe production, simple handling, reduced energy requirement, improvement of the environment, water preparation corresponding to DIN standards, and no corrosion problems with pipes or devices that come into contact with the chlorite-chlorine dioxide solution.

[0017]

In accordance with the invention, chlorite is preferably used. A chlorite salt and especially sodium chlorite ($NaClO_2$), potassium chlorite, magnesium chlorite, calcium chlorite or aluminum chlorite is preferably used as chlorite. Because of its general availability and low cost, sodium chlorite is most preferred, and it is used in particular in an amount from 0.1 to 5 g/m^3. In addition, it was found that when sodium chlorite is used in electrolysis to from chlorine dioxide byproducts are formed only in very small amounts, if at all. To reduce the formation of byproducts that can possibly have an adverse affect on water treatment or water disinfection, and to reduce the absolute content of byproducts, a chlorite that is as pure as possible should be used. Chlorite with a minimum purity of 80% is advantageously used. If a chlorate is used, sodium chlorate ($NaClO_3$) is preferred.

[0018]

The electrolysis of the chlorite solution can be carried out under standard conditions, where the use of metal electrodes coated with noble metals or metal electrodes coated with combinations of various noble metals as anode and cathode for the method in accordance with the invention has proved to be advantageous. The elements, alloys and/or compounds that are usually used for electrodes can be used here. For purposes of the invention iron and titanium electrodes have proved to be especially advantageous, and titanium electrodes are especially preferred. As an example, in accordance with the invention an electrolysis solution (i.e., the water to be treated), to which 1 g of chlorite has been added per cubic meter of water, is used.

[0019]

The electrolysis is then carried out at currents from 1 to 8 amperes, preferably about 4 amperes, and a voltage of about 9 volts, where chlorine dioxide is formed in amounts sufficient for disinfection, -from 0.1 to 0.15 mg/L. The current can be supplied from a substantially known commercially available control unit.

[0020]

The electrolysis can be carried out continuously or at intervals, as required. A concentration of up to 2.0 mg chlorine dioxide per liter of water to be treated is to be seen as sufficient for the quality of the water to correspond to DIN Standard 19643-1.

[0021]

In a preferred embodiment of the method in accordance with the invention the water to be treated and containing the chlorite and/or chlorate is kept in circulation. This means that a part of

the water is continuously or at intervals passed through an electrolysis cell and there the chlorite is electrolytically converted to chlorine dioxide, so that a predetermined chlorine dioxide concentration is continuously and constantly present in the water being treated. For this a part of the water can be removed, passed through an electrolysis cell, and then sent back. Here it is preferred that chlorine dioxide, which is consumed in the water treatment and/or water disinfection, is at least partially regenerated by electrolysis. It was found that with a circulating system the total amount of chlorite/chlorate and chlorine dioxide practically does not degrade. Only a slight degradation, if at all, was observed. The electrolysis of chlorite to chlorine dioxide which was carried out with high yield and at favorable costs is reversible, if one looks at the chlorite/chlorine dioxide system. When the chlorine dioxide that is formed acts as a disinfectant, it is again reduced to chlorite in the oxidation of microbes. Natural processes of decomposition of the chlorine dioxide in water also result in the formation of chlorite. This chlorite formed from the initially electrolytically produced chlorine dioxide can then again be regenerated electrolytically to chlorine dioxide.

[0022]

In an especially preferred embodiment it is thus possible in accordance with the invention for the chlorite concentration to be established through the addition of a specific amount of chlorite, and no further addition of chlorite will be necessary in the course of the process over a long period of time of around, for example ½ year, preferably 1 year. Through the regeneration, or reverse conversion, of chlorite to chlorine dioxide and vice versa, continuous addition of further sodium chlorite is not necessary. Rather the chlorine dioxide formed in the electrolysis is converted back to chlorite, especially sodium chlorite, through microbes or other mechanisms, so that the amount of chlorite itself in the water practically does not degrade or undergoes only negligible degradation.

[0023]

The electrolysis is preferably carried out so that the chlorine dioxide is present in the water in a concentration from 0.05 to 0.2 ppm, especially in a concentration from 0.09 to 0.11 ppm. In this amount the chlorine dioxide already has a disinfectant effect, but does not yet have any deleterious side effects. An odor of chlorine dioxide resembling chlorine and ozone is not perceivable until a level of about 5 ppm is reached and chlorine dioxide attacks the mucosa only at a concentration of about 45 ppm.

[0024]

A further improvement of the method in accordance with the invention can be obtained through the addition of stabilizers for chlorine dioxide, so that the energy required for electrolysis is reduced further. For example, chlorine dioxide can be stabilized through addition of pyridine, so that preferably pyridine is added to the water to be treated in low concentrations, for example up to 1 ppm.

[0025]

It is additionally possible to add other additives to the water in addition to chlorite. In particular, the use of a mixture of chlorite and chloride, for example about 20 to 50 g sodium chlorite and about 1 kg sodium chloride, has proven to be advantageous.

[0026]

The method in accordance with the invention is especially suitable for water disinfection of swimming pools, especially private swimming pools, since it is easy to set up, toxic side effects do not arise, and it is not necessary to handle dangerous chemicals. Through the formation of chlorine dioxide in the filter system permanently clear and hygienic swimming pool water can be produced without continuous maintenance. The amount of chlorite can be preset at the start of a season of use and will not then have to be continuously supplemented by the user.

[0027]

Preferably, the amount of chlorite is preset so that no makeup is necessary during a summer period of swimming pool use.

[0028]

The invention is illustrated in more detail by the accompanying Figure 1, in which the circulation of the water to be treated is shown. The water drawn from the pool by a pump is optionally passed through a filter and then passed through a continuously or discontinuously operating electrolysis cell, in which the chlorite is converted to chlorine dioxide. The water containing chlorine dioxide then flows back through a pipe to the pool. The pump and the electrolysis cell can be controlled by an electronic control device, for example as a function of the measured water quality and/or chlorine dioxide concentration.

Claims

1. A method for water treatment and/or water disinfection using chlorine dioxide, which is characterized by the fact that chlorine dioxide is electrolytically produced from chlorite and/or

chlorate, which are present in a preset concentration from 0.1 to 5 ppm, in the water that is to be treated.

2. A method as in Claim 1, which is characterized by the fact that a part of the water that is to be treated and that contains chlorite and/or chlorate is continuously removed or removed at intervals, subjected to a hydrolysis, and then returned.

3. A method as in Claim 1 or 2, which is characterized by the fact that chlorine dioxide, which has been consumed in the water treatment and/or water disinfection, is at least partially electrolytically regenerated.

4. A method as in one of the preceding claims, which is characterized by the fact that chlorine dioxide is produced in the water to be treated in a concentration from 0.05 to 0.2 ppm.

5. A method as in one of the preceding claims, which is characterized by the fact that a stabilizer for chlorine dioxide is additionally added.

6. A method as in one of the preceding claims, which is characterized by the fact that chloride is additionally added to the water to be treated.

7. The use of the method as in one of the preceding claims to treat and/or disinfect swimming pool water.

8. A use as in Claim 7, which is characterized by the fact that no makeup takes place in the course of a summer period.

1 Drawing Attached

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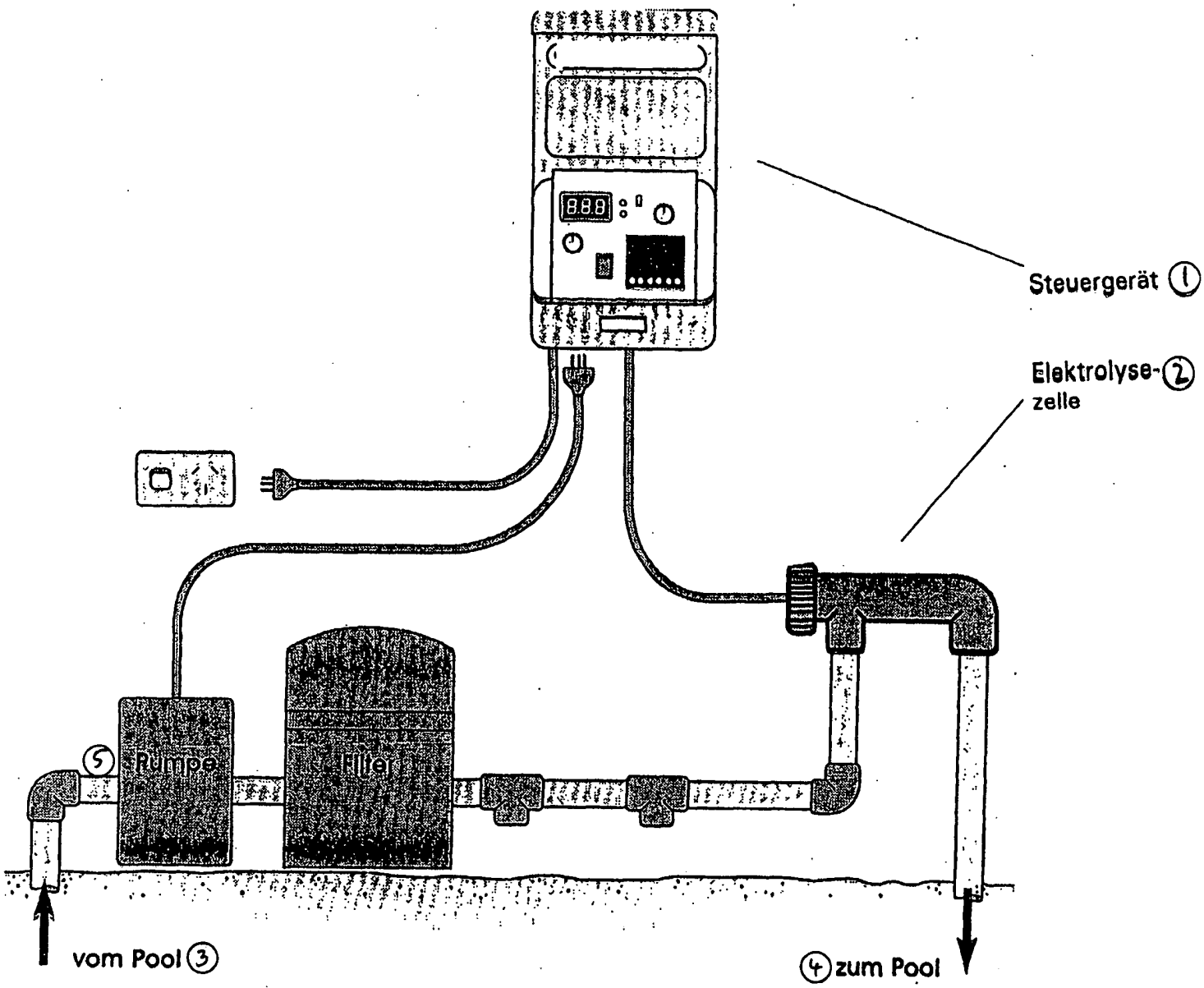

Figure 1

Key:
1 Control device
2 Electrolysis cell
3 To pool
4 From pool
5 Pump